Synthesis and Some Transformations of 5-Benzotriazolyl-3,4-dihydropyrid-2-ones

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5-(Benzotriazolyl)-substituted 3,4-dihydropyrid-2-ones were obtained by condensation of 4-benzotriazolyl-5-phenyl(methyl)-5-oxopentanoic acids with benzyl or aryl amines. Dehydrogenation of 3,4-dihydropyrid-2-ones resulted in 5-benzotriazolyl-substituted pyrid-2-ones and/or 5-(phenylamino)pyrid-2-ones, products of nitrogen elimination from the benzotriazolyl substituent. In turn, 5-benzotriazol-1-yl-substituted pyrid-2-ones eliminated nitrogen under Graebe-Ullmann conditions to give indolopyridones.

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Introduction.

The pyrid-2-one moiety is found in numerous naturally occurring compounds including alkaloids and other physiologically active products [1]. One approach to pyrid-2-ones involves the dehydrogenation of 3,4-dihydropyrid-2-ones [2], and routes to the latter are therefore of interest. The most general syntheses of 3,4-dihydropyrid-2-ones comprise (i) reactions of 5-oxopentanoic acids or pyran-2-ones with ammonia or amines [3,4], (ii) interaction of enamines with acrylic acid derivatives [5,6] and (iii) reactions of 1-azabutadienes with enolates of substituted acetates [7], with acrylates [8], or with ketenes [9]. Other approaches include reactions of aromatic ketimines with acrylic acid derivatives [10,11], 1,4-addition of methylene ketones to methacrylamides [12], Beckmann-type rearrangement of unsaturated *N*-methylnitrones [13], and hydrocarbonylation of alkenamides [14]. The efficiency of all these reactions depends upon the availability of the corresponding starting materials. We have not found any published data on the synthesis of 3,4-dihydropyrid-2-ones with an aromatic heterocycle as a substituent in the pyridone ring.

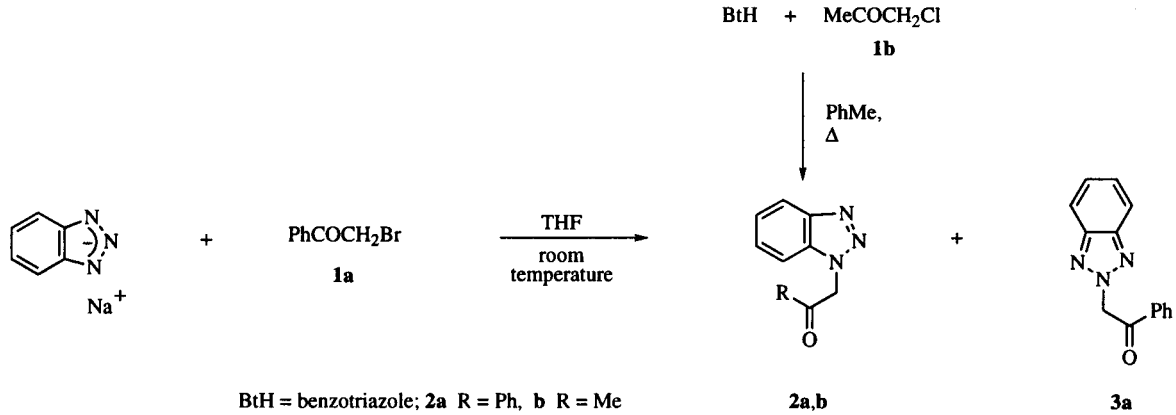
We now report a convenient synthesis of 5-benzotriazolyl-substituted 3,4-dihydropyrid-2-ones and their dehydrogenation accompanied by the benzotriazole ring destruction, as well as the application of the Graebe-Ullmann reaction to 5-(benzotriazol-1-yl)pyrid-2-ones.

Results and Discussion.

It is well known that the sodium salt of benzotriazole can be *N*-alkylated with α-halogeno ketones or alkyl halides to give mixtures of benzotriazol-1-yl and -2-yl derivatives [15,16]. The isomers can be separated [16], or used as a mixture for further transformations [15]. We employed this method for the synthesis of the isomeric mixture of α-(benzotriazolyl)acetophenones **2a** and **3a** (Scheme 1) which were separated for further reactions [16]. We reported recently that if the alkylation of benzotriazole with α-halogeno carbonyl compounds was carried out in refluxing toluene, the only product was the benzotriazol-1-yl isomer [17]: we applied this technique for the synthesis of (benzotriazol-1-yl)acetone **2b** (Scheme 1).

α-Benzotriazol-1-yl ketones **2a,b** were alkylated with ethyl acrylate under conditions of phase-transfer catalysis [18] followed by *in situ* hydrolysis of the ester group to give δ-oxo carboxylic acids **4a,b** (Scheme 2) in 70% and

Scheme 1

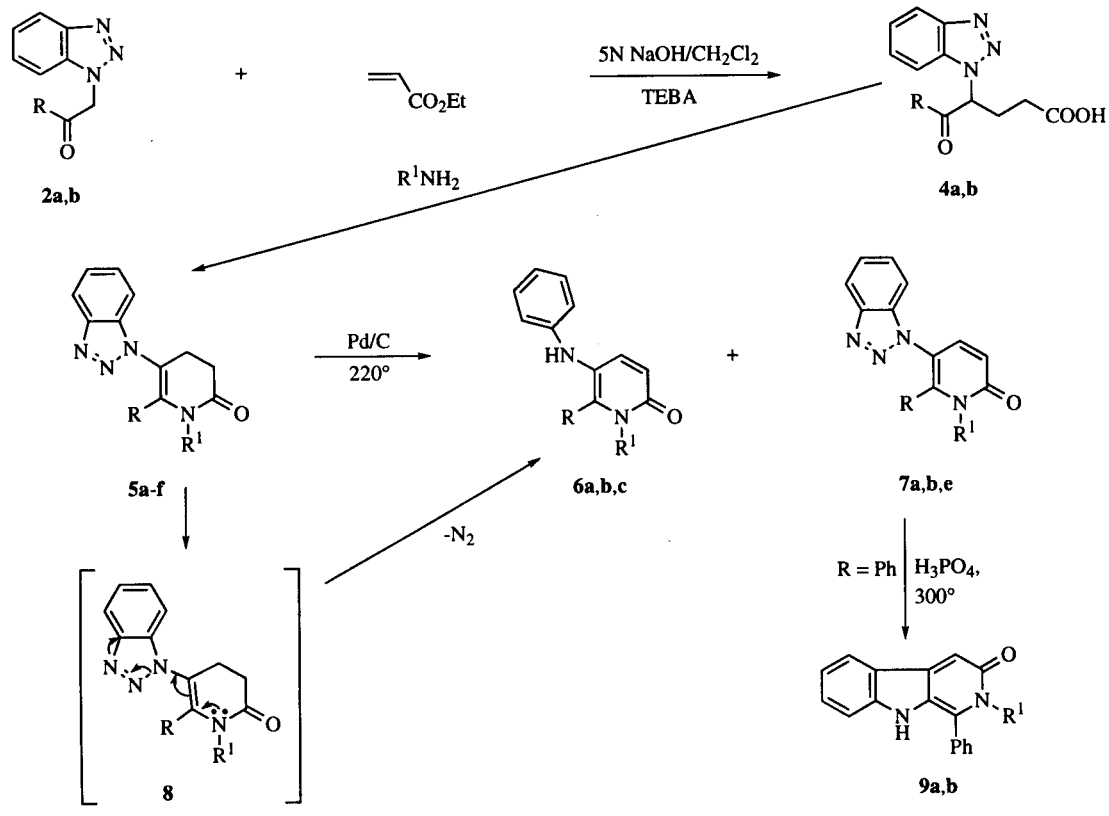


BtH = benzotriazole; **2a** R = Ph, **b** R = Me

2a,b

3a

Scheme 2



4a R = Ph; **b** R = Me; **5-7a** R = R^1 = Ph; **b** R = Ph, R^1 = 4-MeC_6H_4; **c** R = Ph, R^1 = 4-$MeOC_6H_4$; **d** R = Ph, R^1 = CH_2Ph; **e** R = Me, R^1 = Ph; **f** R = Me, R^1 = 4-MeC_6H_4; **9a** R^1 = Ph; **b** R^1 = 4-MeC_6H_4

85% yields, respectively. The ^1H nmr spectra of compounds **4a,b** showed signals characteristic of the methene aliphatic proton as a double doublet at δ 6.81 and 5.69, respectively. The methylene groups appeared at ~ δ 2.80-2.20 as two multiplets of two protons each for **4a**, and as four multiplets of one proton each for **4b**. The interaction of acids **4a,b** with primary amines smoothly resulted in 5-(benzotriazol-1-yl)-3,4-dihydropyrid-2-ones **5a-f** in 56-88% yields. The ^1H nmr spectra of compounds **5a-f** revealed the signals of the two methylene groups as multiplets at ~ δ 2.90-3.20.

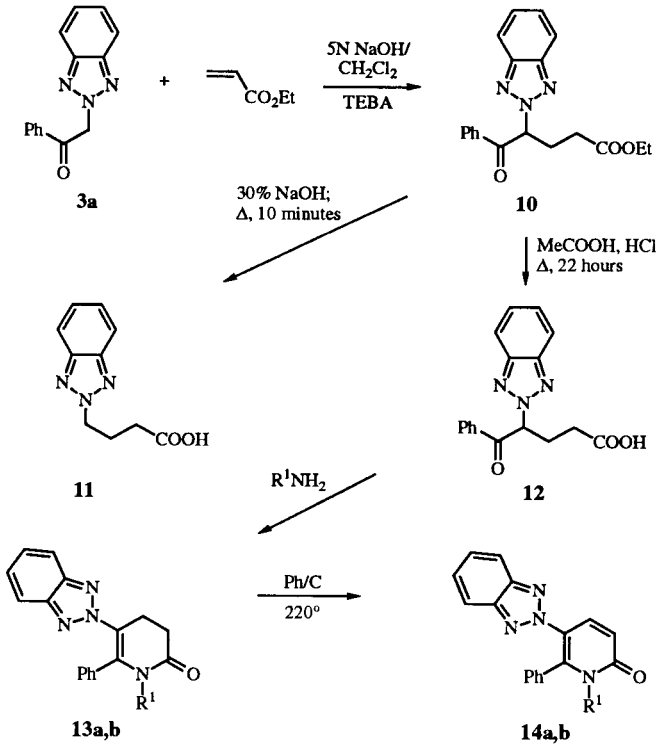
Dehydrogenation of some 3,4-dihydropyrid-2-one derivatives to pyrid-2-ones reportedly proceeded on refluxing in tetralin in the presence of 10% palladium on carbon [2]. Under these conditions, however, dehydrogenation of **5a-f** did not occur. On heating neat 3,4-dihydropyrid-2-one **5e** with 10% palladium on carbon under nitrogen at 220° for 2 hours, the pyridone **7e** was formed in 85% yield, whereas on dehydrogenation of **5a,b**, mixtures of 5-(benzotriazol-1-yl)pyrid-2-ones **7a,b** with the corresponding 5-(phenylamino)pyrid-2-ones **6a,b** were isolated. The ratios of compounds **6** and **7** in the mixtures depended upon the electron-donating effect of the substituent at the nitrogen atom in the dihydropyridone ring of **5**: more pronounced electron donation increased the proportion of the 5-(phenylamino)pyrid-2-one **6**, and dehydrogenation of **5c** resulted only in phenylaminopyridone **6c** in 85% yield. The isolated compounds **7** did not give phenylaminopyridones **6** on heating neat with palladium on carbon even for 3 hours, and the starting materials were recovered in 90-95% yields. No formation either of compound **7** or of **6** occurred if dihydropyrid-2-one **5** was heated neat without palladium on carbon. Thus, the mechanism of formation of phenylaminopyridones **6** suggests elimination of one molecule of nitrogen from the benzotriazole ring as shown for **8** (Scheme 2) along with intra- or intermolecular transfer of two hydrogen atoms which occurred in the presence of palladium on carbon. The ^1H nmr spectra of both pyridin-2-ones **6** and **7** revealed the characteristic downfielded signal of the λ-pyridine proton as a doublet at ~ δ 7.50 with J = 9.8 Hz. The signal of the β–pyridine proton was distinguished only for **6a,b** and **7e** at ~ δ 6.70 as a doublet with J = 9.8 Hz. The elimination of nitrogen from the benzotriazole ring was previously

reported on thermolysis in the presence of acids (the Graebe-Ullmann reaction) [19], on photolysis [20], or under conditions of nucleophilic attack [21-23]. We have found no literature examples on elimination of nitrogen from the benzotriazole ring under the general conditions of dehydrogenation.

Heating 5-(benzotriazol-1-yl)pyridin-2-ones **7a,b** in 85% phosphoric acid at 330° for 10 minutes resulted β-carbolinones **9a,b** (Scheme 2) in 35% and 30% yields, respectively. The method employed is a modification of the Graebe-Ullmann carbazole and benz-γ-carboline synthesis [19]. We found no literature data on its application for the synthesis of indolo-2',3':3,4-pyrid-6-ones of type **9**. The few known examples of this class of compounds were obtained by reaction of indolo-α-pyrones with primary amines [24].

Alkylation of (benzotriazol-2-yl)acetophenone **3a** with ethyl acrylate under the conditions used for the benzotriazol-1-yl derivatives **2a,b** (Scheme 2), gave ester **10** (Scheme 3) in 85% yield. Surprisingly, compound **10** did not react with aryl amines even on prolonged refluxing in toluene. The alkali-catalyzed hydrolysis of the ester group in **10** was accompanied by elimination of the benzoyl group, and the acid **11** was isolated in 60% yield. The desired δ-oxo carboxylic acid **12** was obtained on acid-catalyzed hydrolysis of the ester **10** in 75% yield. Similarly to the compounds **4a,b**, interaction of acid **12** with aryl amines gave 5-(benzotriazol-2-yl)-3,4-dihydropyrid-2-ones **13a,b**. As expected, dehydrogenation of **13a,b** smoothly resulted in 5-(benzotriazol-2-yl)pyridin-2-ones **14a,b** as the only products in 82% and 75% yields, respectively.

Scheme 3



13,14 a R^1 = Ph; **b** R^1 = 4-MeC_6H_4

Conclusion.

The interaction of benzotriazol-1-yl and -2-yl-substituted δ-oxo pentanoic acids with primary amines led to the corresponding 5-(benzotriazolyl)-3,4-dihydropyrid-2-ones. Dehydrogenation of benzotriazol-2-yl-substituted 3,4-dihydropyrid-2-ones yielded 5-(benzotriazol-2-yl)-pyrid-2-ones, whereas the same procedure for the benzotriazol-1-yl isomer gave two products: the expected 5-(benzotriazol-1-yl)pyrid-2-ones, and 5-(phenylamino)-pyrid-2-ones, products of the nitrogen elimination from the benzotriazol-1-yl substituent. 5-(Benzotriazol-1-yl)-pyrid-2-ones were transformed into indolopyridones under conditions of the Graebe-Ullmann reaction.

EXPERIMENTAL

Melting points were determined on a Thomas-Hoover capillary melting point apparatus and are uncorrected. The ^1H and ^{13}C nmr spectra were recorded on a Gemini 300 spectrometer (300 and 75 MHz respectively) using deuteriochloroform as solvent (unless otherwise stated) and tetramethylsilane as an internal reference. Flash chromatography was run over EM Science silica gel (230-400 mesh).

(Benzotriazol-1-yl)acetone (**2b**).

A mixture of benzotriazole (1.19 g, 10 mmoles) and bromoacetone (2.05 g, 15 mmoles) in dry toluene (200 ml) was refluxed for 12 hours. The solvent was removed *in vacuo*, and the residue recrystallized from ethanol to give colorless crystals of **2b** (80%), mp 129°; ^1H nmr: δ 8.08 (d, 1H, J = 9.1 Hz), 7.53-7.41 (m, 1H), 7.40-7.36 (m, 2H), 5.45 (s, 2H), 2.21 (s, 3H); ^{13}C nmr: δ 199.8, 145.9, 133.4, 127.9, 124.1, 120.1, 109.0, 56.7, 27.0.

Anal. Calcd. for $C_9H_9N_3O$: C, 61.70; H, 5.18; N, 23.99. Found: C, 61.93; H, 5.23; N, 24.15.

General Procedure for the Synthesis of **4a,b**.

A mixture of the corresponding ketone (4.1 mmoles), ethyl acrylate (4.1 mmoles), methylene chloride (10 ml), 5*N* sodium hydroxide aqueous solution and a catalytic amount of tetrabutylammonium hydrogensulfate was stirred at room temperature for 24 hours. Water (15 ml) was added, the organic layer was separated and the aqueous layer was extracted with methylene chloride (2 x 10 ml). The aqueous layer was acidified with concentrated hydrochloric acid to *p*H 6 and the product formed was extracted with methylene chloride (3 x 15 ml). The combined organic extracts obtained by extraction of the acidified aqueous solution were dried over anhydrous sodium sulfate, and the solvent was evaporated *in vacuo* to give the crude product.

3-(Benzotriazol-1-yl)-4-benzoylbutyric Acid (**4a**).

This compound was obtained as colorless microcrystals in

80% yield, mp 156-157° (from benzene); ^{1}H nmr: δ 8.03-8.01 (m, 3H), 7.58-7.32 (m, 6H), 6.81 (dd, 1H, J_1 = 5.4 Hz, J_2 = 9.6 Hz), 2.84-2.62 (m, 2H), 2.44-2.23 (m, 2H) (the signal of the carboxylic proton was not detectable); ^{13}C nmr: δ 193.1, 177.0, 146.3, 134.2, 132.3, 129.0, 128.8, 128.1, 124.5, 120.2, 110.4, 62.5, 29.5, 25.1 (two signals of the aromatic carbon atoms coalesced).

Anal. Calcd. for $C_{17}H_{15}N_3O_3$: C, 66.01; H, 4.89; N, 13.58. Found: C, 66.39; H, 4.92; N, 13.78.

3-(Benzotriazol-1-yl)-4-acetylbutyric Acid (**4b**).

This compound was obtained as colorless microcrystals in 85% yield, mp 121-123° (from ether); ^{1}H nmr: δ 9.40 (br s, 1H), 8.13 (d, 1H, J = 8.3 Hz), 7.56-7.41 (m, 3H), 5.69 (dd, 1H, J_1 = 5.1 Hz, J_2 = 10.1 Hz), 2.84-2.66 (m, 1H), 2.64-2.52 (m, 1H), 2.44-2.33 (m, 1H), 2.25-2.20 (m, 1H), 2.04 (s, 3H); ^{13}C nmr: δ 201.9, 176.3, 145.5, 132.7, 128.2, 124.6, 119.8, 109.5, 66.4, 29.4, 26.7, 24.3.

Anal. Calcd. for $C_{12}H_{13}N_3O_3$: C, 58.29; H, 5.30; N, 16.99. Found: C, 58.35; H, 5.38; N, 16.59.

Ethyl 3-(Benzotriazol-2-yl)-4-benzoylbutyrate (**10**).

A mixture of the corresponding ketone (1.0 g, 4.1 mmoles), ethyl acrylate (0.41 g, 4.1 mmoles), methylene chloride (10 ml), 5*N* sodium hydroxide aqueous solution and a catalytic amount of tetrabutylammonium hydrogensulfate was stirred at room temperature for 24 hours. Water (15 ml) was added, the organic layer was separated and the aqueous layer was extracted with methylene chloride (2 x 10 ml). The combined organic extracts were dried over anhydrous sodium sulfate and the solvent was evaporated *in vacuo* to give **10** (85%), mp 107-108° (colorless crystals from ethanol); ^{1}H nmr: δ 8.09-8.06 (m, 2H), 7.88-7.85 (m, 2H), 7.54-7.45 (m, 1H), 7.43-7.35 (m, 4H), 6.70 (dd, 1H, J_1 = 4.9 Hz, J_2 = 9.8 Hz), 4.14 (q, 2H, J = 7.1 Hz), 2.85-2.77 (m, 2H), 2.52-2.40 (m, 1H), 2.27-2.22 (m, 1H), 1.23 (t, 3H, J = 7.1 Hz); ^{13}C nmr: δ 192.2, 172.4, 144.6, 133.9, 128.83, 128.79, 126.6, 118.3, 68.8, 60.7, 29.8, 26.5, 14.1 (two signals of the aromatic carbon atoms coalesced).

Anal. Calcd. for $C_{19}H_{19}N_3O_3$: C, 67.64; H, 5.68; N, 12.45. Found: C, 67.76; H, 5.64; N, 12.41.

4-(Benzotriazol-2-yl)butyric Acid (**11**).

A mixture of **10** (0.34 g, 1 mmole) and 10% sodium hydroxide aqueous solution (5 ml) was refluxed for 2 hours, cooled and acidified with concentrated hydrochloric acid to *p*H 7. The precipitate formed was extracted with methylene chloride (2 x 10 ml), the combined organic layers were dried over anhydrous sodium sulfate and the solvent was evaporated *in vacuo*. The residue was recrystallized three times from ethanol to give colorless crystals of **11** (60%), mp 110-113°; ^{1}H nmr: δ 10.38 (br s, 1H), 7.88-7.85 (m, 2H), 7.39-7.36 (m, 2H), 4.87-4.83 (m, 2H), 2.46-2.41 (m, 4H); ^{13}C nmr: δ 177.8, 144.2, 126.4, 117.9, 55.3, 30.6, 24.8.

Anal. Calcd. for $C_{10}H_{11}N_3O_2$: C, 58.53; H, 5.40; N, 20.48. Found: C, 58.48; H, 5.48; N, 20.51.

3-(Benzotriazol-2-yl)-4-benzoylbutyric Acid (**12**).

A mixture of **10** (1.0 g, 3 mmoles), glacial acetic acid (7 ml) and concentrated hydrochloric acid (0.5 ml) was refluxed for 22 hours, cooled and diluted with water (10 ml). The precipitate formed was filtered off, washed with water (5 ml), dried and recrystallized from benzene to give colorless crystals of **12** (75%), mp 161°; ^{1}H nmr (dimethyl sulfoxide-d_6): δ 8.02 (d, 2H, J = 7.6 Hz), 7.96-7.93 (m, 2H), 7.66-7.61 (m, 1H), 7.54-7.44 (m, 4H), 6.92 (t, 1H, J = 7.1 Hz), 2.64-2.56 (m, 2H), 2.44-2.33 (m, 1H), 2.27-2.16 (m, 1H) (the signal of the carboxylic proton was not detectable); ^{13}C nmr (dimethyl sulfoxide-d_6): δ 192.8, 173.4, 143.9, 134.3, 134.1, 129.0, 128.5, 126.7, 118.1, 68.7, 29.8, 26.4.

Anal. Calcd. for $C_{17}H_{15}N_3O_3$: C, 66.01; H, 4.89; N, 13.58. Found: C, 65.78; H, 5.05; N, 13.47.

General Procedure for the Synthesis of **5a-f** and **13a,b**.

A mixture of the appropriate acid **4a,b** or **12** (10 mmoles), amine (11 mmoles) and toluene (30 ml) was refluxed with the Dean-Stark adapter (20 ml volume) for 24 hours. The mixture was cooled, the crystalline precipitate was filtered off, washed with diethyl ether (10 ml) and recrystallized from ethanol.

5-(Benzotriazol-1-yl)-1,6-diphenyl-3,4-dihydropyrid-2-one (**5a**).

This compound was obtained as colorless needles in 75% yield, mp 257-258°; ^{1}H nmr: δ 7.92 (d, 1H, J = 8.2 Hz), 7.35-7.14 (m, 5H), 7.10-7.04 (m, 3H), 6.91-6.86 (m, 2H), 6.82-6.78 (m, 3H), 3.18-3.03 (m, 4H); ^{13}C nmr: δ 169.3, 145.1, 142.3, 137.7, 132.8, 131.2, 129.0, 128.8, 128.5, 128.3, 127.61, 127.56, 127.3, 123.8, 119.8, 115.8, 109.4, 32.4, 25.6.

Anal. Calcd. for $C_{23}H_{18}N_4O$: C, 75.39; H, 4.95; N, 15.29. Found: C, 75.71; H, 5.03; N, 15.52.

5-(Benzotriazol-1-yl)-1-(4-methylphenyl)-6-phenyl-3,4-dihydropyrid-2-one (**5b**).

This compound was obtained as colorless needles in 80% yield, mp 208-209°; ^{1}H nmr: δ 7.90 (d, 1H, J = 8.3 Hz), 7.34-7.20 (m, 3H), 6.97 (s, 4H), 6.92-6.87 (m, 2H), 6.82-6.78 (m, 3H), 3.17-3.02 (m, 4H), 2.17 (s, 3H); ^{13}C nmr: δ 169.4, 145.0, 142.4, 137.0, 135.0, 132.7, 131.3, 129.1, 129.0, 128.5, 128.2, 127.54, 127.49, 123.7, 119.7, 115.5, 109.4, 32.4, 25.6, 20.9.

Anal. Calcd. for $C_{24}H_{20}N_4O$: C, 75.77; H, 5.30; N, 14.73. Found: C, 75.93; H, 5.33; N, 14.76.

5-(Benzotriazol-1-yl)-1-(4-methoxyphenyl)-6-phenyl-3,4-dihydropyrid-2-one (**5c**).

This compound was obtained as colorless needles in 56% yield, mp 178°; ^{1}H nmr: δ 7.91 (d, 1H, J = 8.2 Hz), 7.32-7.23 (m, 3H), 6.99 (d, 2H, J = 8.8 Hz), 6.90-6.81 (m, 5H), 6.69 (d, 2H, J = 8.8 Hz), 3.67 (s, 3H), 3.17-3.03 (m, 4H); ^{13}C nmr: δ 169.6, 158.3, 145.1, 142.6, 132.8, 131.3, 130.4, 129.9, 129.1, 128.3, 127.64, 127.56, 123.8, 119.8, 115.4, 113.8, 109.4, 55.2, 32.4, 25.6.

Anal. Calcd. for $C_{24}H_{20}N_4O_2$: C, 72.71; H, 5.08; N, 14.13. Found: C, 72.94; H, 5.03; N, 14.13.

5-(Benzotriazol-1-yl)-1-benzyl-6-phenyl-3,4-dihydropyrid-2-one (**5d**).

This compound was obtained as colorless needles in 88% yield, mp 161°; ^{1}H nmr: δ 7.87 (d, 1H, J = 8.6 Hz), 7.35-7.21 (m, 6H), 7.04-6.89 (m, 7H), 4.47 (m, 2H), 3.07-3.02 (m, 2H), 2.94-2.88 (m, 2H); ^{13}C nmr: δ 169.7, 145.0, 142.6, 137.2, 132.8, 130.5, 129.0, 128.8, 128.3, 128.0, 127.5, 127.1, 127.0, 123.7, 119.8, 115.9, 109.3, 46.5, 31.9, 25.2.

Anal. Calcd. for $C_{24}H_{20}N_4O$: C, 75.77; H, 5.30; N, 14.73. Found: C, 75.80; H, 5.42; N, 14.81.

5-(Benzotriazol-1-yl)-6-methyl-1-phenyl-3,4-dihydropyrid-2-one (**5e**).

This compound was obtained as colorless microcrystals in 78% yield, mp 175°; ^{1}H nmr: δ 8.11 (d, 1H, J = 8.3 Hz), 7.59-7.54 (m, 1H), 7.50-7.39 (m, 5H), 7.28-7.25 (m, 2H), 3.08-3.03 (m, 2H), 2.97-2.91 (m, 2H), 1.40 (s, 3H); ^{13}C nmr: δ 169.3, 145.5, 137.6, 137.4, 133.2, 129.4, 128.8, 128.4, 128.1, 124.2, 120.3, 113.8, 109.6, 31.9, 25.1, 16.3.

Anal. Calcd. for $C_{18}H_{16}N_4O$: C, 71.04; H, 5.30; N, 18.41. Found: C, 71.08; H, 5.36; N, 18.61.

5-(Benzotriazol-1-yl)-6-methyl-1-(4-methylphenyl)-3,4-dihydropyrid-2-one (**5f**).

This compound was obtained as colorless needles in 85% yield, mp 144-145°; ^{1}H nmr: δ 8.12 (d, 1H, J = 8.2 Hz), 7.59-7.54 (m, 1H), 7.46-7.40 (m, 2H), 7.28 (d, 2H, J = 8.0 Hz), 7.14 (d, 2H, J = 8.2 Hz), 3.09-3.03 (m, 2H), 2.96-2.91 (m, 2H), 2.39 (s, 3H), 1.40 (s, 3H); ^{13}C nmr: δ 169.5, 145.5, 138.4, 137.6, 135.0, 133.3, 130.1, 128.6, 128.1, 124.2, 120.3, 113.5, 109.6, 32.0, 25.1, 21.1, 16.3.

Anal. Calcd. for $C_{19}H_{18}N_4O$: C, 71.68; H, 5.70; N, 17.60. Found: C, 71.55; H, 5.82; N, 17.64.

5-(Benzotriazol-2-yl)-1,6-diphenyl-3,4-dihydropyrid-2-one (**13a**).

This compound was obtained as colorless prisms in 78% yield, mp 182-184° dec; ^{1}H nmr: δ 7.74-7.70 (m, 2H), 7.33-7.29 (m, 2H), 7.20-7.15 (m, 2H), 7.10-7.04 (m, 3H), 6.95-6.90 (m, 5H), 3.26-3.21 (m, 2H), 3.17-3.12 (m, 2H); ^{13}C nmr: δ 169.4, 144.1, 141.0, 137.7, 131.7, 129.4, 129.1, 128.5, 128.2, 127.6, 127.3, 126.7, 121.8, 118.0, 32.2, 25.6.

Anal. Calcd. for $C_{23}H_{18}N_4O$: C, 75.39; H, 4.95; N, 15.29. Found: C, 75.48; H, 5.18; N, 15.09.

5-(Benzotriazol-2-yl)-1-(4-methylphenyl)-6-phenyl-3,4-dihydropyrid-2-one (**13b**).

This compound was obtained as colorless plates in 75% yield, mp 225-226° dec; ^{1}H nmr: δ 7.72-7.69 (m, 2H), 7.55-7.27 (m, 2H), 6.90-6.88 (m, 9H), 3.25-3.19 (m, 2H), 3.15-3.09 (m, 2H), 2.18 (s, 3H); ^{13}C nmr: δ 169.5, 144.1, 141.1, 137.1, 135.1, 131.8, 129.4, 129.2, 128.8, 128.1, 127.5, 126.6, 121.6, 118.0, 32.1, 25.6, 21.0.

Anal. Calcd. for $C_{24}H_{20}N_4O$: C, 75.77; H, 5.30; N, 14.73. Found: C, 75.38; H, 5.23; N, 14.63.

General Procedure for the Synthesis of **6a,b,c**, **7a,b,e** and **14a,b**.

A mixture of the appropriate dihydropyridone **5** or **13** (2 mmoles) and 10% palladium on carbon (0.16 g) was stirred at 220° under nitrogen for 2 hours. The mixture was cooled, treated with methylene chloride (200 ml) and the palladium on carbon was filtered off. The filtrate was evaporated *in vacuo* and the residue was treated with diethyl ether (70 ml) to give the crude pyridones **7a,b,e** and **14a,b** from **5a,b,e** and **13a,b**, respectively, which were filtered off and recrystallized from ethanol. The ethereal filtrate was evaporated *in vacuo* to give crude **6a,b,c** from **5a,b,c**, respectively, which were purified by flash column chromatography (silica gel, methylene chloride-methanol,40: 1).

1,6-Diphenyl-5-(phenylamino)pyrid-2-one (**6a**).

This compound was obtained as yellow microcrystals in 20% yield, mp 103-105°; ^{1}H nmr: δ 7.55 (d, 1H, J = 9.7 Hz), 7.24-7.09 (m, 8H), 7.05-7.03 (m, 2H), 6.98-6.95 (m, 2H), 6.86-6.79 (m, 1H), 6.73 (d, 1H, J = 9.8 Hz), 6.67 (d, 2H, J = 8.5 Hz), 4.82 (s, 1H); ^{13}C nmr: δ 161.8, 145.6, 141.7, 140.0, 138.7, 131.9, 129.6, 129.3, 128.9, 128.7, 128.5, 128.2, 127.8, 120.9, 120.8, 119.6, 114.9.

Anal. Calcd. for $C_{23}H_{18}N_2O$: C, 81.63; H, 5.36; N, 8.28. Found: C, 81.58; H, 5.44; N, 8.31.

5-(Benzotriazol-1-yl)-1,6-diphenylpyrid-2-one (**7a**).

This compound was obtained as colorless needles in 70% yield, mp 248-250° dec; ^{1}H nmr: δ 7.93 (d, 1H. J = 8.5 Hz), 7.55 (d, 1H, H = 9.8 Hz), 7.41-7.36 (m, 1H), 7.31-7.20 (m, 5H), 7.12 (d, 2H, J = 7.8 Hz), 6.91-6.82 (m, 6H); ^{13}C nmr: δ 162.3, 149.0, 145.1, 139.2, 137.8, 133.9, 130.2, 129.0, 128.93, 128.89, 128.8, 128.4, 127.9, 127.6, 124.0, 120.9, 119.9, 115.8, 109.3.

Anal. Calcd. for $C_{23}H_{16}N_4O$: C, 75.81; H, 4.43; N, 15.37. Found: C, 75.48; H, 4.57; N, 15.06.

1-(4-Methylphenyl)-6-phenyl-5-(phenylamino)pyrid-2-one (**6b**).

This compound was obtained as yellow microcrystals in 40% yield, mp 108-110°; ^{1}H nmr: δ 7.53 (d, 1H, J = 9.7 Hz), 7.20-7.11 (m, 5H), 7.01-6.92 (m, 6H), 6.84-6.78 (m, 1H), 6.72 (d, 1H, J = 9.8 Hz), 6.65 (d, 2H, J = 8.0 Hz), 4.81 (s, 1H), 2.21 (s, 3H); ^{13}C nmr: δ 162.0, 145.7, 142.0, 139.9, 137.6, 136.1, 132.0, 129.6, 129.4, 129.3, 128.52, 128.46, 128.2, 120.8, 120.7, 119.5, 114.9, 21.0.

Anal. Calcd. for $C_{24}H_{20}N_2O$: C, 81.79; H, 5.72; N, 7.95. Found: C, 81.59; H, 5.74; N, 7.82.

5-(Benzotriazol-1-yl)-1-(4-methylphenyl)-2-phenylpyrid-2-one (**7b**).

This compound was obtained as light brown plates in 50% yield, mp 233-235°; ^{1}H nmr: δ 7.92 (d, 1H, J = 8.2 Hz), 7.54 (d, 1H, J = 9.7 Hz), 7.40-7.35 (m, 1H), 7.30-7.26 (m, 2H), 7.06 (d, 2H, J = 8.5 Hz), 6.98 (d, 2H, J = 8.8 Hz), 6.91-6.83 (m, 6H), 2.24 (s, 3H); ^{13}C nmr: δ 162.5, 149.2, 145.1, 139.1, 138.4, 135.2, 133.9, 130.3, 129.6, 129.0, 128.8, 128.4, 127.9, 127.6, 123.9, 120.8, 119.9, 115.7, 109.3, 21.1.

Anal. Calcd. for $C_{24}H_{18}N_4O$: C, 76.17; H, 4.79; N, 14.80. Found: C, 75.96; H, 4.88; N, 14.64.

1-(4-Methoxyphenyl)-6-phenyl-5-(phenylamino)pyrid-2-one (**6c**).

This compound was obtained as yellow microcrystals in 85% yield, mp 103-105°; ^{1}H nmr: δ 7.51 (d, 1H, J = 9.8 Hz), 7.18-7.10 (m, 5H), 6.98-6.92 (m, 4H), 6.85-6.75 (m, 2H), 6.71-6.23 (m, 4H), 4.90 (s, 1H), 3.66 (s, 3H); ^{13}C nmr: δ 161.9, 158.5, 145.6, 142.3, 139.9, 131.9, 131.3, 129.6, 129.4, 129.1, 128.3, 128.1, 127.5, 120.6, 119.3, 114.7, 113.8, 55.0.

Anal. Calcd. for $C_{24}H_{20}N_2O_2$: C, 78.24; H, 5.47; N, 7.60. Found: C, 78.00; H, 5.54; N, 7.41.

5-(Benzotriazol-1-yl)-6-methyl-1-phenylpyrid-2-one (**7e**).

This compound was obtained as light brown prisms in 85% yield, mp 188-189°; ^{1}H nmr: δ 8.16 (d, 1H, J = 8.3 Hz), 7.61-7.41 (m, 6H), 7.32-7.25 (m, 3H), 6.71 (d, 1H, J = 9.7 Hz), 1.74 (s, 3H); ^{13}C nmr: δ 162.7, 146.1, 145.6, 138.6, 138.0, 134.0, 130.1, 129.4, 128.6, 127.7, 124.5, 120.4, 119.1, 115.4, 109.4, 17.2.

Anal. Calcd. for $C_{18}H_{14}N_4O$: C, 67.92; H, 4.43; N, 17.60.

Found: C, 67.97; H, 4.51; N, 17.63.

5-(Benzotriazol-2-yl)-1,5-diphenylpyrid-2-one (**14a**).

This compound was obtained as light brown plates in 82% yield, mp 210-213° dec; ^{1}H nmr: δ 7.75 (d, 1H, J = 9.8 Hz), 7.75-7.72 (m, 2H), 7.34-7.24 (m, 5H), 7.10-7.07 (m, 2H), 6.99-6.93 (m, 5H), 6.84 (d, 1H, J = 9.7 Hz); ^{13}C nmr: δ 162.3, 144.6, 138.2, 137.9, 130.7, 129.4, 129.0, 128.7, 128.4, 127.6, 127.0, 122.3, 120.4, 118.1 (two signals of the aromatic carbon atoms coalesced with other signals).

Anal. Calcd. for $C_{23}H_{16}N_4O$: C, 75.81; H, 4.43; N, 15.37. Found: C, 75.58; H, 4.48; N, 14.98.

5-(Benzotrizol-2-yl)-1-(4-methylphenyl)-6-phenylpyrid-2-one (**14b**).

This compound was obtained as light brown microcrystals in 75% yield, mp 225-227° dec; ^{1}H nmr: δ 7.73 (d, 1H, J = 9.7 Hz), 7.71-7.74 (m, 2H), 7.33-7.30 (m, 2H), 7.07-6.93 (m, 9H), 6.82 (d, 1H, J = 9.8 Hz), 2.24 (s, 3H); ^{13}C nmr: δ 162.4, 147.5, 144.5, 138.3, 138.1, 135.2, 130.8, 129.6, 129.4, 128.6, 128.5, 127.5, 126.9, 122.2, 120.2, 118.1, 21.1.

Anal. Calcd. for $C_{24}H_{18}N_4O$: C, 76.17; H, 4.79; N, 14.80. Found: C, 76.18; H, 4.53; N, 14.89.

General Procedure for the Synthesis of **9a,b**.

A mixture of pyrid-2-one **7** (15 mmoles) and 85% phosphoric acid (1.5 ml) was heated under stirring at 330° until vigorous elimination of nitrogen was completed (*ca.* 10 minutes). The mixture was cooled, treated with water (20 ml) and extracted with methylene chloride (3 x 10 ml). The organic extracts were dried over anhydrous sodium sulfate, and the solvent was removed *in vacuo*. The residue was recrystallized from dimethyl formamide to give **9**.

1,2-Diphenyl(indolo-2',3':3,4-pyrid-6-one) (**9a**).

This compound was obtained as dark orange microcrystals in 35% yield, mp >300° dec; ^{1}H nmr: δ 7.92 (d, 1H, J = 8.0 Hz), 7.53 (d, 2H, J = 9.8 Hz), 7.32-7.05 (m, 9H), 6.90-6.80 (m, 4H); ^{13}C nmr: δ 162.4, 149.0, 145.5, 145.1, 139.3, 129.9, 129.2, 128.9, 128.8, 128.7, 128.6, 128.53, 128.46, 128.0, 127.6, 124.0, 120.8, 119.9, 109.3.

Anal. Calcd. for $C_{23}H_{16}N_2O$: C, 82.12; H, 4.79; N, 8.33. Found: C, 82.00; H, 4.83; N, 8.21.

1-(4-Methylphenyl)-2-phenyl(indolo-2',3':3,4-pyrid-6-one) (**9b**).

This compound was obtained as dark orange microcrystals in 30% yield, mp >320° dec; ^{1}H nmr: δ 7.90 (d, 1H, J = 7.8 Hz), 7.43-6.93 (m, 14H), 2.21 (s, 3H); ^{13}C nmr: δ 161.8, 145.5, 142.0, 139.9, 137.6, 136.4, 130.8, 129.9, 129.5, 129.34, 129.29, 128.9, 128.7, 128.6, 125.6, 123.1, 119.6, 111.0, 106.0, 21.1.

Anal. Calcd. for $C_{24}H_{18}N_2O$: C, 82.26; H, 5.18; N, 7.99. Found: C, 82.10; H, 5.21; N, 7.82.

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